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TECHNICAL REPORT BRL-TH-2921

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**CRITICAL EVALUATION OF THE OSCILLATOR  
STRENGTHS OF NH<sub>2</sub> AND THE HEATS  
OF FORMATION OF NH AND NH<sub>2</sub>**

**WILLIAM R. ANDERSON**

**JULY 1988**

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  BRL-TR-2921			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION US Army Ballistic Research Laboratory		6b. OFFICE SYMBOL (If applicable)  SLCBR-IB	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code)  Aberdeen Proving Ground, MD 21005-5066			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO. 61102A	PROJECT NO. AH43	TASK NO.
			WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) CRITICAL EVALUATION OF THE OSCILLATOR STRENGTHS OF NH <sub>2</sub> AND THE HEATS OF FORMATION OF NH AND NH <sub>2</sub>					
12. PERSONAL AUTHOR(S) WILLIAM R. ANDERSON					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM Sep 85 to Sep 87		14. DATE OF REPORT (Year, Month, Day)	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	NH Radical, NH <sub>2</sub> Radical, Oscillator Strengths, Heats of Formation, amines. (Nirgu) ←		
07	04				
20	05				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The NH and NH <sub>2</sub> radicals are expected to be of importance in the combustion chemistry of double base and nitramine propellants. It is therefore worthwhile to have spectroscopic probes for these radicals both for the flames which simulate the propellant combustion zone and for the propellant itself. However, the database for NH <sub>2</sub> spectroscopy lacks absolute values for the absorption oscillator strengths of NH <sub>2</sub> . A method has recently been presented for the calculation of these oscillator strengths. In this paper a critical comparison of calculated oscillator strengths with the few measurements which exist is made. Promising agreement is found with reliable measurements. Further experiments are recommended to test the technique since there is presently scant data of sufficient quality to test the calculational method. During the course of these comparisons, it was found that results of the measurements depend heavily on the values chosen for the heats of formation of NH and NH <sub>2</sub> . Since these quantities have long been the subject of considerable debate, a critical literature survey was performed. During the course of the survey, several recent papers					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL DR. WILLIAM R. ANDERSON			22b. TELEPHONE (Include Area Code) 301-278-7070		22c. OFFICE SYMBOL SLCBR-IB-1

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

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19. Abstract (Cont'd):

were published with precision limits much better than previous results. These have greatly facilitated the present comparison of oscillator strengths. After critical examination of all pertinent papers in the literature, the values recommended for the NH and NH<sub>2</sub> heats of formation (0°K) are 85.4±0.3 and 45.9±0.2 kcal/mole, respectively.

# PREFACE

Note concerning units:

Throughout this paper, the following conversions are used:

$$1 \text{ kcal} = 4.184 \text{ kJ}$$

$$1 \text{ eV} = 23.061 \text{ kcal} = 96.49 \text{ kJ}$$

$$1 \text{ cm}^{-1} = 1.2398 \times 10^{-4} \text{ eV} = 2.8591 \times 10^{-3} \text{ kcal/mole} = 1.196 \times 10^{-2} \text{ kJ/mole}$$

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## I. INTRODUCTION

The nitrogen chemistry which takes place in the combustion of double-base and nitramine propellants is of particular interest to us. The  $\text{NH}$  and  $\text{NH}_2$  radicals are expected to play a key role in this chemistry. Both of these radicals have been observed in several  $\text{N}_2\text{O}$  supported flames<sup>1-3</sup> and in  $\text{NH}_3$  flames.<sup>1,3,4</sup> Since  $\text{N}_2\text{O}$  is believed to be an important intermediate in the combustion of these propellants,<sup>5</sup>  $\text{NH}$  and  $\text{NH}_2$  are also expected to be present. However, it is not certain whether the  $\text{NH}_x$  species play a major role in determining the heat release rates and flame speeds of  $\text{N}_2\text{O}$  supported flames. These species are expected to play a central role in HCN flames via the sequence  $\text{HCN} \rightarrow \text{CN} \rightarrow \text{NCO} \rightarrow \text{NH}_x \rightarrow \text{N}_2$  (or perhaps  $\text{NO}$ ). This sequence is believed to be responsible for the conversion of fuel-bound nitrogen (that is, N atoms bonded to C atoms, as in coal) to  $\text{N}_2$  and, more importantly,  $\text{NO}_x$  pollutants.<sup>6</sup> HCN is known to be formed in large quantities during the pyrolysis of nitramine propellants.<sup>5</sup> Therefore, it is important to have quantitative detection methods for the  $\text{NH}$  and  $\text{NH}_2$  species. These methods are expected to be valuable for studies of the chemistry of flames involving HCN,  $\text{H}_2\text{CO}$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$  in a low pressure apparatus which we are currently assembling.

Laser induced fluorescence (LIF)<sup>1-4</sup> and absorption spectroscopies<sup>2,7-10</sup> can be used to detect both  $\text{NH}$  and  $\text{NH}_2$  in flames. However, in the past it has proven difficult to measure  $\text{NH}_2$  densities quantitatively because no method was available to calculate Einstein coefficients or oscillator strengths for individual rovibronic lines of the most readily observed transition,  $\tilde{A}^2A_1 - \tilde{X}^2B_1$ .<sup>11</sup> In fact, the previous best estimates of oscillator strengths for individual  $\text{NH}_2$  lines have error limits<sup>9</sup> of about a factor of 10! The difficulty stems in large part from the fact that the molecule is a highly bent asymmetric rotor in its ground state and becomes nearly linear in its excited state. We have recently studied LIF of  $\text{NH}_2$  in several  $\text{N}_2\text{O}$  supported flames.<sup>3</sup> During the course of this work a simple method for calculating the oscillator strengths of main branch transitions of  $\text{NH}_2$  was developed. The calculated oscillator strengths were then used in a measurement of the  $\text{NH}_2$  density in an  $\text{H}_2/\text{N}_2\text{O}/\text{N}_2$  flame. However, several simplifying assumptions were made in the oscillator strength calculations. The accuracy of the calculations was therefore somewhat uncertain.

In the present work, a comparison of calculated  $\text{NH}_2$  oscillator strengths with values from the few measurements which exist is made. The experimental values all come from absorption measurements of several species in  $\text{NH}_3/\text{O}_2$  flames in which chemical equilibria are set up between the  $\text{NH}_x$  species. In the course of this study it became apparent, not surprisingly, that the experimental values are somewhat sensitive to the assumed heats of formation of the species involved in the chemical equilibria. The heats of formation of  $\text{NH}_2$  and, in particular,  $\text{NH}$  were not precisely known at the onset of this study\*. (Heats of formation of the other species are well established).

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\*This study began about Sep 1985. At the inception of the study, the  $\text{NH}$  and  $\text{NH}_2$  heats of formation could not be pinpointed to within better than a few kcal/mole. Since that time, several very precise measurements have appeared which have greatly facilitated this study.

Therefore, a critical review of these two heats of formation has been performed. The review will be presented herein. As a result of this work, these two heats of formation are now precisely established. In some of the previous oscillator strength measurements, incorrect values were used for these heats of formation in the data reduction. The measured oscillator strengths are corrected in the present work. A comparison of measured and calculated strengths is given. The agreement looks good where the measurements can be trusted, but there are so few measurements that further experiments will be needed to thoroughly assess the reliability of the calculated values. Some suggestions for such experiments are given.

## II. NH<sub>2</sub> OSCILLATOR STRENGTH CALCULATION

Einstein A emission coefficients were first calculated for transitions of interest and then converted to oscillator strengths. The procedure has been presented previously<sup>3</sup> and is discussed briefly here. The A coefficients are obtained from the equation:

$$A_{v',v''}^{N',N''} = |\mu_e^0|^2 \left( \frac{64\pi^4}{3h} \right) \left( \frac{S_{N',N''}}{2N'+1} \right) \langle v' | \sin(\rho/2) | v'' \rangle^2 \Delta v_{v',v''}^3$$

where  $\mu_e^0$  is the limiting transition moment at the bending angle  $\rho = 180^\circ$  (Note:  $\rho = 0$  in the linear limit as defined in Ref. 12),  $S_{N',N''}$  is the rotational linestrength,  $\langle v' | \sin(\rho/2) | v'' \rangle^2$  is the vibronic transition moment (VTM) for the  $(0,v',0) - (0,v'',0)$  band of interest, and  $\Delta v_{v',v''}$  is the vibrational transition energy. Lifetime measurements from three sources<sup>13-15</sup> have been analyzed in Ref. 15 to yield  $|\mu_e^0|^2 = (0.094 \pm 0.010)e^2 a_0^2$ , where  $e$  is electronic charge and  $a_0$  is the Bohr radius. This result compares well with the theoretical value,<sup>16</sup>  $0.10e^2 a_0^2$ . The experimental result is used for our calculations. VTMs are obtained from the semi-empirical calculations of Jungen, Hallin, and Merer.<sup>12</sup> (Recently, Peric, et al.,<sup>17</sup> reported nearly identical results using an ab initio approach. The potentials they used were from Jungen, Hallin, and Merer's work). Our major contribution to the calculation is the rotational linestrengths. These linestrengths were calculated using the direction cosine matrix elements of Cross, et al.,<sup>18</sup> and the eigenvectors resulting from the diagonalization of a Wang transformed asymmetric top Hamiltonian.<sup>19,20</sup> It is to be stressed here that the ground and excited state asymmetry parameters are not assumed to be the same (equivalent to assuming that the ground and excited state bending angles are the same, which is decidedly not true) as has been done in all previous linestrength calculations for this molecule.\* In fact, the excited state constants are appropriate for a linear molecule. However, two major assumptions are made. First, spin splitting of the lines is ignored. That is

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\*We have recently discovered that calculated linestrengths for three transitions are given in Ref. 21. They are 1.00, 3.48, and 2.38 for lines emitted from the  $3_{03}$  upper state level in the  $(0,9,0)E - (0,0,0)$  band (lines unspecified). We find the same results, to three significant digits, if we assume these are for the  $R_{1,N-1}$ ,  $Q_{1,N}$ , and  $P_{1,N-1}$  transitions, respectively. No details as to calculational procedures or assumptions were given.



why the line strengths are referred to as  $S_{N',N''}$  rather than  $S_{J',J''}$ . This assumption is permissible if strong Hund's case b states are involved in the transition, as in the present case. The assumption obviously, however, restricts us to the calculation only of main branch transitions. An entire main branch doublet must be scanned in an experiment, or one must assume oscillator strengths for the two lines in a given doublet are nearly equal, which appears to be the case.<sup>3</sup> The second assumption is that the electronic transition moment has no large variation with rotational or vibrational levels. In addition to these assumptions, the reader is cautioned to note that the calculation is not expected to work well for transitions that involve perturbed levels. In spite of these restrictions, this method allows the calculation of oscillator strengths for a large number of transitions which may be useful for probing this molecule. The resulting oscillator strengths are generally of the order of  $10^{-4}$  for main branch transitions.

### III. HEATS OF FORMATION

There presently exists little experimental data of sufficient quality to yield measured  $\text{NH}_2$  oscillator strengths which can be compared with our calculated results. Most of the data which exists comes from measurements in  $\text{NH}_3/\text{O}_2$  flames. It has been shown using absorption measurements that the reactions:



are in equilibrium in the burnt gas region of these flames.<sup>7,8,10</sup> Kaskan and Nadler<sup>7b</sup> also convincingly demonstrated the equilibration of these reactions using an electrical analog of a simplified reaction mechanism. Note that the third reaction is the sum of the first two so that equilibration of the first two necessarily implies equilibration of the third. All of the species involved in these reactions, except  $\text{H}_2\text{O}$  whose concentration may be reliably inferred from the fuel/oxidizer ratio, can be measured in absorption. Oscillator strengths are presently well known for all of the species except  $\text{NH}_2$ . Most of the necessary thermal data are precisely known. However, the heats of formation of  $\text{NH}_2$  and, especially,  $\text{NH}$  have historically been subjects of considerable debate. Since these quantities are extremely important to the present comparison of measured and calculated  $\text{NH}_2$  oscillator strengths, a critical literature survey of these heats of formation was performed. Results of the survey are given in the next two subsections. It was found that the heats of formation of both radicals may be firmly established within a few tenths of a kcal/mole using results of very recent experiments.

#### A. $\text{NH}_2$ :

Results of the survey for heat of formation of  $\text{NH}_2$  are given in Tables 1-3. In this section, we shall first discuss recommendations and measurements from early work. These studies lead to the conclusion that the heat of formation of  $\text{NH}_2$  must be about 46 kcal/mole. More recent papers will then be discussed. The results of two recent papers, Gibson, et al.,<sup>37</sup> and Sutherland

and Michael,<sup>39</sup> have much higher precision than all of the others (See Table 1). These two papers are considered by this author to be the best measurements currently available and are equally valid. These papers are in outstanding agreement with one another. As will be seen in the next section, the results of Ref. 37 for the  $\text{NH}_2$  heat of formation also can be used to derive an  $\text{NH}^+$  heat of formation that is in excellent agreement with results obtained by other methods. In addition, the two results are in reasonable agreement with recent theoretical calculations (See Table 2). After critical evaluation, their weighted average,  $45.9 \pm 0.2$  kcal/mole, is chosen as the best available value for the heat of formation of  $\text{NH}_2$ .

Table 1. Measured Values for the Heat of Formation of  $\text{NH}_2^*$

Reference	$\Delta H_{f,0}^\circ$ (kcal/mole)
Szwarc (1949) <sup>22-24</sup>	$42 \pm 3$
Foner and Hudson (1958) <sup>25</sup>	$45 \pm 3$
Page (1961) <sup>26</sup>	$40 \pm 3$
Kerr, et al. (1963) <sup>27</sup>	39.8
Compton, et al. (1969) <sup>28</sup>	$39 \pm 3$ ( $< 41.4 \pm 3.5$ )
Golden, et al. (1972) <sup>29</sup>	$47.9 \pm 2$
Kurylo, et al. (1969) <sup>30</sup> as interpreted by Golden, et al. <sup>29</sup>	47
Bohme, et al. (1973) <sup>31</sup>	$45.0 \pm 1.1$
Carson, et al. (1977) <sup>32</sup>	$48.8 \pm 3.5$
Tsang (1978) <sup>33</sup>	$44.7 \pm 1.9$
DeFrees, et al. (1979) <sup>34</sup>	$44.7 \pm 2.3$
Niemitz, et al. (1981) <sup>35</sup>	47
Holzrichter and Wagner (1981) <sup>36</sup>	$46.8 \pm 3.1$
Gibson, et al. (1985) <sup>37</sup>	$45.8 \pm 0.3$
Hack, et al. (1986) <sup>38</sup>	$46.6$ ( $\pm 1.7$ )
Sutherland and Michael (1986) <sup>39</sup>	$46.0 \pm 0.3$

\*Numbers given in parenthesis were derived in the present work.

Table 2. Theoretical Values for the Heat of Formation of  $\text{NH}_2$

Reference	$\Delta H_{f,0}^\circ$ (kcal/mole)
Altshuller (1954) <sup>40</sup>	$41 \pm 2$
Jordan and Longuet-Higgins (1962) <sup>41</sup>	41.2
Bews and Glidewell (1980) <sup>42</sup>	30.08
Cardy, et al. (1980) <sup>43</sup>	43
Bischof and Friedrich (1982) <sup>44</sup>	36.6
Klimo and Tino (1983) <sup>45</sup>	47.1
Power, et al. (1984) <sup>46</sup>	54.5
Melius and Binkley (1986) <sup>47</sup>	46.7

Table 3. Recommended Values for the Heat of Formation of  $\text{NH}_2$

Reference	$\Delta H_{f,0}^\circ$ (kcal/mole)
JANAF (1965) <sup>a,48</sup>	40.8±3
Wagman, et al. (1965) <sup>b,49</sup>	44.9
Benson and O'Neal (1970) <sup>50</sup>	43.3±3
JANAF (1977) <sup>b,51</sup>	46.2±1.5
Glushko, et al. (1978) <sup>52</sup>	46.1±2.4
This work	45.9±0.2

a. Published in open literature in 1977.

b. Published in open literature in 1982.

Until about 1965, the heat of formation of  $\text{NH}_2$  was believed to be about 40 kcal/mole (See Table 3). This result was based primarily on kinetic measurements of the activation energy for the dissociation of hydrazine and several amines to yield  $\text{NH}_2$  (Szwarc;<sup>22-24</sup> Kerr, et al.<sup>27</sup>). Here, the assumption is, of course, that the activation energy for the reverse reaction of two radicals to form the parent molecule is zero (within about 2 kcal/mole). However, in 1970 Benson and O'Neil<sup>50</sup> pointed out that under the conditions used in these experiments, these unimolecular decompositions were almost surely in the pressure fall-off region. Upon reinterpreting the kinetics results they recommended a somewhat higher value, 43.3±3 kcal/mole. Wagman, et al.,<sup>49</sup> apparently arrived at the same conclusion in 1965 since they recommend a value of 44.9 kcal/mole, although no explanation is given as to how this value was selected. The JANAF review<sup>51</sup> of 1977 and the Russian review (Glushko, et al., Ref. 52) both recommend a value of about 46±2 kcal/mole, based upon much the same line of reasoning. The former also gives citations<sup>53,54</sup> in which Hinshelwood-Lindemann and RRKM theories were used to conclusively prove that the decomposition studies were performed in the pressure falloff region. All of the measurements from 1972 on are in good agreement with this value (See Table 1). Of particular note is the result, 47.9±2 kcal/mole, of Golden, et al.,<sup>29</sup> obtained from kinetics measurements on benzylamine decomposition using their very low pressure pyrolysis technique. The results were again interpreted using RRKM theory.

Several other points should be made here in regards to Table 1. First, the result of Foner and Hudson<sup>25</sup> obtained using ionization and appearance potential measurements in mass spectrometric experiments appears to support the JANAF recommendation. However, this result should be viewed with some skepticism because, as will be discussed later, the values obtained for the ionization potential of  $\text{NH}_2$  and the appearance potential of  $\text{NH}_2^+$  are probably both about 5-6 kcal/mole too high. These errors cancel, yielding a heat of formation of  $\text{NH}_2$  in fortuitous agreement with the recommended value. Second, consider the result of Compton, et al.<sup>28</sup> This result was obtained from an electron impact study of the reaction  $\text{NH}_3 + e^- \rightarrow \text{NH}_2 + \text{H}^-$ . Following Piper,<sup>55</sup> one may write  $E_{in} > \Delta H_{f,0}^\circ(\text{NH}_2) + \Delta H_{f,0}^\circ(\text{H}^-) - \Delta H_{f,0}^\circ(\text{NH}_3) - 3/2RT$ . (The last term was ignored by Compton, et al.). Here, the  $E_{in}$  term is the threshold energy for observation of the reaction which was observed to be 3.65 eV.

Using the established heats of formation<sup>51</sup> of H and NH<sub>3</sub> and the electron affinity<sup>56</sup> of H, 51.643, -9.3 and 17.4 kcal/mole, respectively, and noting that the experiment was performed at room temperature, we find an upper limit of 41.6±3.5 kcal/mole for the heat of formation of NH<sub>2</sub>. The upper end of this range is in much closer agreement with the JANAF recommendation than the original interpretation of Compton, et al. Finally, consider the recent result of Hack, et al.<sup>38</sup> Here, kinetics measurements were performed for the reaction NH<sub>2</sub> + H<sub>2</sub> → NH<sub>3</sub> + H and its reverse. The reaction enthalpy was inferred from the results in two different ways, yielding almost identical results. However, error limits were not given. From the spread in the results of determinations at several different temperatures, the error limits should be about 1.7 kcal/mole.

From the preceding discussion, it is apparent that the heat of formation of NH<sub>2</sub> must be about 46 kcal/mole. Nearly all of the experimental results favor this value. Two of the recent results, that of Gibson, et al.<sup>37</sup> and that of Sutherland and Michael,<sup>39</sup> have remarkably low error limits. These will be discussed in detail in the next two paragraphs.

The result of Gibson, et al., was obtained by photoionization mass spectrometric measurements on NH<sub>2</sub> which was produced by the reaction of H with N<sub>2</sub>H<sub>4</sub>. They measured the ionization potential of NH<sub>2</sub> to be 11.14±0.01 eV. Foner and Hudson<sup>25</sup> and Dunlavey, et al.,<sup>57</sup> found values of 11.4±0.1 and 11.46 eV, respectively, for this quantity, but these values<sup>37</sup> lead to results for the NH<sub>2</sub> heat of formation which are much too low. Note that the former result has very large error limits. The latter value results from a spectrum which has considerable interference from a vibrational progression from ionization of NH<sub>3</sub>. Dunlavey, et al., attempted to subtract the interference, but apparently there is a large error in the result. Gibson, et al., combined their ionization potential of NH<sub>2</sub> with the appearance potential 15.768 ± 0.004 eV for the reaction NH<sub>3</sub> + NH<sub>2</sub><sup>+</sup> + H + e<sup>-</sup> obtained from McCulloh.<sup>58</sup> (Foner and Hudson<sup>25</sup> obtained 16.0±0.1 eV for this appearance potential). They thus obtained 45.8±0.3 kcal/mole for the heat of formation. This heat of formation of NH<sub>2</sub>, combined with other data on ionization and appearance potentials of NH<sub>x</sub><sup>+</sup> species, can be used to derive a value for the heat of formation of NH<sup>+</sup>. This NH<sup>+</sup> heat of formation is in excellent agreement with determinations using a second method, kinetics of the N<sup>+</sup> + H<sub>2</sub> → NH<sup>+</sup> + H reaction (see next section). While cancellation of systematic errors could lead to the observed agreement in results, this possibility seems unlikely.

The results of Sutherland and Michael<sup>39</sup> were obtained by kinetics measurements on the reaction H + NH<sub>3</sub> → H<sub>2</sub> + NH<sub>2</sub>. H atoms were made by photolyzing NH<sub>3</sub> in a shock tube. The H atom concentration was followed by Lyman alpha absorption. Its disappearance follows pseudo first order kinetics. Note that at initial time, the H and NH<sub>2</sub> concentrations are equal (care was taken to assure this condition). The thermochemical measurement was performed by adding H<sub>2</sub> to the reactive mixture. By varying the NH<sub>3</sub>/H<sub>2</sub> mixture ratio, it was possible to determine the point at which equilibrium is established because at that point the forward and reverse reaction rates are equal and the rate of disappearance of H becomes zero. Since the H atom concentration does not change, the NH<sub>2</sub> concentration will not either. Therefore, the ratio of these concentrations cancels in the equilibrium constant expression leaving only the NH<sub>3</sub>/H<sub>2</sub> ratio which is known. Since heats

of formation for the other species in this reaction are well known, the  $\text{NH}_2$  heat of formation could be readily inferred from the equilibrium constant.

The results of Gibson, et al., and of Sutherland and Michael are in excellent agreement (see Table 1). The most recent theoretical result (Melius and Binkley,<sup>47</sup> see Table 2) is also in reasonable agreement with their results. Since Gibson, et al.'s, result also leads to an  $\text{NH}^+$  heat of formation in excellent agreement with results using other methods, the  $\text{NH}_2$  heat of formation is now firmly established. Results of these two experiments appear to be equally valid. Their weighted average,<sup>59</sup>  $45.9 \pm 0.2$  kcal/mole, is therefore chosen as the recommendation of this critical evaluation for the heat of formation of  $\text{NH}_2$ .

#### B. NH:

Results of the survey for heat of formation of NH are summarized in Tables 4-7. This section is arranged with discussions of previous recommendations first. The recommendations are compared with recent measurements and reinterpretations of results obtained from experiments on  $\text{NH}_3/\text{O}_2$  flames. The results are found to be rather divergent (see Table 4). However, it will then be shown that two papers stand out from those in Table 4 in that they can be used to set firm upper and lower limits on the heat of formation. The first is the high resolution spectroscopic study of the  $\text{NH } c^1\Pi$  state by Graham and Lew.<sup>67</sup> Predissociation observed in this state may be used to set a lower limit of  $84.1 \pm 1.2$  kcal/mole. The second paper is the study of production of NH in the A state via  $\text{NH}_3$  photolysis at 193 nm by Hofzumahaus and Stuhl.<sup>73</sup> In this work the internal energy of the NH produced was measured and then modeled using two assumed prior distributions. No other workers using similar types of dissociation approaches to produce NH have attempted such modeling. This must therefore be considered the best of such types of experiments. The result of these efforts was an upper limit of 87.7 kcal/mole to the heat of formation. Upon inclusion of error limits of these bracketing results, we conclude that the heat of formation must be in the range 82.9 - 88.2 kcal/mole. The experiments of Gibson, et al.,<sup>37</sup> and of Ervin and Armentrout<sup>75</sup> are considered next. These experiments both result first in the determination of very precise results for the heat of formation of the  $\text{NH}^+$  ion. In the respective papers, these results were then combined with the ionization potential of NH to yield very precise values for the heat of formation. Since the results depend so heavily on this ionization potential, a review of available measurements is presented herein. After critical review, it was found that the best value is that of Dunlavey, et al.,<sup>57</sup>  $13.49 \pm 0.01$  eV, which was used in Refs. 37 and 75. The heats of formation given for NH in Refs. 37 and 75 are believed to be the best available measurements. It will be shown that they are in excellent agreement with each other, have much smaller error limits than any other results, are in reasonable agreement with the best recent theoretical results, and fall at the center of the range delimited by less precise results. Since these two measurements are considered to be equally correct, their weighted average,  $85.4 \pm 0.3$  kcal/mole, is selected as the best value for the heat of formation of NH presently available. At the end of this section, the results of Ref. 10 are discussed in regards to this value.

Table 4. Measured Values for the Heat of Formation of NH (Excluding Results from NH<sub>3</sub>/O<sub>2</sub> Flame Equilibria)\*

Reference	$\Delta H_{f,0}^{\circ}$ (kcal/mole)
Pannettier and Gaydon (1951) <sup>60</sup>	76.6
Franklin, et al. (1958) <sup>61</sup>	81 ( $<83 \pm 3.5$ )
Reed and Sneddon (1959) <sup>62</sup>	82.9 ( $<84.2 \pm 3.5$ )
Seal and Gaydon (1966) <sup>63</sup>	90.1 $\pm$ 3.7
Stedman (1970) <sup>64</sup>	>80
	<94 ( $<83.3 \pm 0.9$ )
Smith, et al. (1976) <sup>65</sup>	>73
Zetzsch (1978) <sup>66</sup>	<84.6
Graham and Lew (1978) <sup>67</sup>	>84.1 $\pm$ 1.2
Okabe (1978) <sup>68</sup>	82.6 $\pm$ 1.5
Okabe and Lenzi (1979) <sup>69</sup> as interpreted by Piper <sup>55</sup>	----- ( $<83.5 \pm 1.4$ )
Xuan, et al. (1981) <sup>70</sup>	<94.6 $\pm$ 2
Quinton and Simons (1982) <sup>71</sup>	<77.1 $\pm$ 1.7
Suto and Lee (1983) <sup>72</sup>	<87.9 $\pm$ 1.4
Hofzumahaus and Stuhl (1985) <sup>73</sup>	<87.7 $\pm$ 0.5
Washida, et al. (1985) <sup>74</sup>	90.2 - 91.3
Gibson, et al. (1985) <sup>37</sup>	85.2 $\pm$ 0.4
Ervin and Armentrout (1987) <sup>75</sup>	85.8 $\pm$ 0.6

\*Results in parentheses are from the reanalyses by Piper.<sup>55</sup>

Table 5. Heat of Formation of NH from Measurements on NH<sub>3</sub>/O<sub>2</sub> Flame Equilibria

Reference	$\Delta H_{f,0}^{\circ}$ (kcal/mole)		
	Original Analysis	Piper's Analysis <sup>55</sup>	This Analysis
Kaskan and Nadler (1972) <sup>7</sup>	90 $\pm$ 4	86.9 $\pm$ 3.9	86.6 $\pm$ 3.9
Fisher (1977) <sup>8</sup>	90.3 $\pm$ 3		86.3 $\pm$ 1.4
Chou, et al. (1982-4) <sup>10</sup>	~87	flame 1 flame 3	87.6 $\pm$ 1.2 89.4 $\pm$ 1.2

Table 6. Recent Theoretical Results for the Heat of Formation of NH\*

Reference	$\Delta H_{f,0}^\circ$ (kcal/mole)
Meyer and Rosmus (1975) <sup>86</sup>	85.8±1.2
Klimo and Tino (1983) <sup>45</sup>	86.5
Power, et al. (1984) <sup>46</sup>	92.5
Melius and Binkley (1986) <sup>47</sup>	86.9
Bauschlicher and Langhoff (1987) <sup>87</sup>	86.5±0.7

\*Earlier results may be found in Refs. 40, 41, and 76-85.

Table 7. Recommended Values for the Heat of Formation of NH

Reference	$\Delta H_{f,0}^\circ$ (kcal/mole)
JANAF (1965) <sup>a,48</sup>	81.0±2.5
Wagman, et al. (1965) <sup>b,49</sup>	83.9
JANAF (1977) <sup>b,51</sup>	90±4
Glushko, et al. (1978) <sup>52</sup>	81.0±2.4
Piper (1979) <sup>55</sup>	84.2±2.3
Hofzumahaus and Stuhl (1985) <sup>73</sup>	84.2 - 88.2
This work	85.4±0.3

a. Published in open literature in 1977.

b. Published in open literature in 1982.

As can be seen from Table 4, the heat of formation of NH has long been a subject of considerable controversy with measured values ranging from about 73-95 kcal/mole. Recommended values (See Table 7) up to 1978 ranged from about 80-90 kcal/mole. The excellent critical review by Piper<sup>55</sup> in 1979 served to bring some accord among the many diversant results available at that time. He recommends a value of 84.2±2.3 kcal/mole. Several results have been obtained by measurements of species involved in reaction R3 in NH<sub>3</sub>/O<sub>2</sub> flames (see Table 5). (Note that this approach does not depend on the heat of formation of NH<sub>2</sub>). The result of Kaskan and coworkers<sup>7</sup> was revised by Piper<sup>55</sup> since a much better choice for the oscillator strength of OH became available. (A more recent review<sup>88</sup> of this oscillator strength supports Piper's choice). A further slight correction of the result has been made for the oscillator strength of NH by the present author. (The oscillator strength used corresponds to a lifetime of 450±45 ns for the A<sup>3</sup>Π state of NH. This value was obtained by averaging the results of 5 lifetime measurements.<sup>65,89-92</sup> Since the correction to the NH heat of formation was performed, two new, very precise measurements of the lifetime have been performed in which very low

rotational levels were excited. Recent results of Garland and Crosley<sup>93</sup> are  $418 \pm 4$  ns for  $N'=1$ ,  $v'=0$  while Browarzik and Stuhl<sup>94</sup> find  $423 \pm 15$  ns for a mixture of a few levels of low  $N'$ :  $N'=1-4$ ,  $v'=0$ . A critical survey<sup>95</sup> of these lifetime measurements has concluded that these are the best values available. Since these results fall within error limits of the value chosen for the present calculations, use of the new value would produce almost identical results in the heat of formation calculations.) The result of Fisher<sup>8</sup> has similarly been revised by the present author for oscillator strengths of both OH and NH. The revised results are within error limits of Piper's recommendation, although they are somewhat on the high side (see Tables 5 and 7). However, Chou, Dean, and Stern<sup>10</sup> found a value of "about" 87 kcal/mole. A careful reanalysis using their measured concentrations for two flames leads to the results shown in Table 5. (Results for their flame 2 were not used because of probable systematic errors discussed in Ref. 10c). The average of these two results is  $88.5 \pm 1.5$  kcal/mole.\* This result and that of Washida, et al.,<sup>74</sup> agree better with the most recent JANAF recommendation than with Piper's recommendation, clouding the picture somewhat.

The proper value to select for the NH heat of formation may be bracketed by consideration of the spectroscopic results. A firm lower limit may be established by considering the predissociation limit of NH in the  $c''$  state. The study of Graham and Lew<sup>67</sup> yields  $84.1 \pm 1.2$  kcal/mole. This result must be considered a lower limit because there may be a barrier to the predissociation  $NH + hv \rightarrow N + H$ . Although Zetzsch<sup>66</sup> finds essentially the same result, he has incorrectly concluded this approach yields an upper limit and he fails to place error limits on the result. Note that the internal energy of the predissociating NH is well known from the spectroscopic results while no reasonable energetics allow for excitation of the atomic species. Internal energies of the three species involved are therefore well defined and do not cloud the interpretation of results for this reaction.

Upper limits for the NH heat of formation may be obtained by examining the energetics of dissociation reactions which produce NH. Whereas internal energies of reactants in the predissociation of NH are well known, this in general has not been the case for studies of the dissociation of suitable precursors to yield NH as a product because the NH may carry away significant vibrational and rotational energy. This problem is compounded by the fact that NH observed in highly excited states following the dissociation may result from highly excited states of the precursor molecule. Thermodynamic quantities therefore cannot be confidently calculated simply by considering which is the highest level of NH observable (assuming a fixed dissociation energy source is used). It is thus necessary to have a model for the

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\*It is important to note that since R3 was used to obtain this heat of formation, the result does not depend on the oscillator strength chosen for  $NH_2$ . It can be shown that if one writes simultaneous equations for equilibria of reactions R1 and R2 treating  $\Delta H_{f,0}^{\circ}(NH)$  and the oscillator strength of  $NH_2$  as unknowns, the results are independent from one another, contrary to the implications of Ref. 10c. This is the case because the sum of R1 and R2 is R3.



distribution of internal energies in the products in order to make a sensible thermodynamic analysis. Such an analysis was provided recently by Hofzumahaus and Stuhl<sup>73</sup> in their study of the ArF laser (193 nm) photolysis of  $\text{NH}_3$ . The reaction studied was  $\text{NH}_3 + 2h\nu \rightarrow \text{NH}(\text{A}^3\Pi) + \text{H} + \text{H}$ . The NH A state distribution was determined by dispersing the emission. The measured distribution was then fitted to obtain the NH heat of formation using two prior distributions, the first with six degrees of freedom, the second with three. Strangely, it was found that the distribution with three degrees of freedom fit the observed data better than that with six. (Hofzumahaus and Stuhl suggest this indicates that one of the H atoms produced is translationally very cold.) The upper limits to the heat of formation were 85.6 and 87.7 kcal/mole for assumptions of six and three active degrees of freedom, respectively. Since the latter model fits the data best, 87.7 kcal/mole was the choice of Hofzumahaus and Stuhl. (Curiously, as shall be seen later, the former is in much better agreement with the final recommendation of this review than the latter). Again, there may be a barrier to the dissociation so that this result must be an upper limit to the heat of formation.

Upon considering the error limits in the two selected limiting values one concludes that the heat of formation of NH must be in the range 82.9 - 88.2 kcal/mole. Only a few of the results in Table 4 do not agree with this range. The result of Pannetier and Gaydon<sup>60</sup> was from a Birge-Sponer extrapolation of NH vibrational levels. Such extrapolations frequently yield large errors in the results. Although Seal and Gaydon<sup>63</sup> state that no emission of NH was observed in their shock tube/absorption studies on H/N/O systems, experiments under similar conditions by Harrington, et al.,<sup>96</sup> indicated large amounts of NH emission are present. If appreciable emission was present in Seal and Gaydon's experiments, the resulting heat of formation would be too large. In any case, their results, with their large error limits, do overlap our suggested range. Yet, as will be seen later, their result does not quite overlap the final recommendation of the present work. Perusal of the spread in results given in Seal and Gaydon's Figure 4 suggests the error limits may have been slightly underestimated. Quinton and Simons<sup>71</sup> studied vacuum ultraviolet photodissociation of  $\text{NH}_3$  using a tunable uv source and filtered photomultiplier detection of NH ( $\text{c}^1\Pi$ ). They also used an atomic O resonance lamp (130.4 nm) and dispersed the NH emission. The threshold for observation of NH provided the thermochemical result in the case of the tunable uv source. For the dispersed emission experiments with the atomic resonance lamp, the same information was obtained by considering the highest rotational level observed. They obtain an upper limit of 77.1 kcal/mole. Observations of Washida, et al.,<sup>74</sup> make it clear that a small amount of atomic H, if present in the discharge lamp, could give rise to a heat of formation much too low for the resonance lamp results. It is not clear why the tunable source results might be in error. Perhaps emission from some other species besides NH was observed in these experiments. In any case, the predissociation results on the NH  $\text{c}^1\Pi$  state make it clear that the result of Quinton and Simons is much too low. Washida, et al., repeated the O atom resonance lamp experiments using a filter to block the H Lyman  $\alpha$  line and found that no NH ( $\text{c}^1\Pi$ ) was formed at all. Further results using other atomic lines led them to a value of 90.2 - 91.3 kcal/mole for the heat of formation. This result must be considered an upper limit like all of the other experiments in which some precursor was dissociated to yield excited NH. It is therefore in agreement with the range suggested here. Finally, it should

be pointed out that the agreement of results of Reed and Sneddon,<sup>62</sup> as reinterpreted by Piper,<sup>55</sup> with the present recommendation is fortuitous. As will be seen later, Reed and Sneddon's appearance potential of  $\text{NH}^+$  from  $\text{NH}_3$  is questionable. In addition, the ionization potential of  $\text{NH}$  used by Piper has been superseded by more recent, better measurements (see later). The errors in these quantities cancel in the data analysis.

Recent experiments of Gibson, et al.,<sup>37</sup> and of Ervin and Armentrout<sup>75</sup> have yielded very precise determinations of the  $\text{NH}$  heat of formation (see Table 4). Both groups also calculated the  $\text{NH}^+$  heat of formation prior to the  $\text{NH}$  heat of formation. These results are considered to be the best presently available. They are therefore discussed in some detail in the next few paragraphs.

As discussed in the last section, the result of Gibson, et al., was obtained by photoionization mass spectrometric experiments. Their result for the  $\text{NH}^+$  heat of formation was  $396.3 \pm 0.3$  kcal/mole. This value was obtained by combining their  $\text{NH}_2$  heat of formation with the appearance potential for the process  $\text{NH}_2 + \text{NH}^+ + \text{H} + \text{e}^-$  which they found to be  $17.440 \pm 0.005$  eV. Reed and Sneddon<sup>62</sup> had previously found  $17.1 \pm 0.1$  eV for an  $\text{NH}^+$  appearance potential in the same region by electron impact measurements on  $\text{NH}_3$ . Little detail is given concerning the latter measurement, but the precision is clearly low and perhaps less than claimed. In addition, the process responsible for  $\text{NH}^+$  production was assigned as  $\text{NH}_3 + \text{NH}^+ + \text{H}_2 + \text{e}^-$ . This latter process has an energy of about 17.6 eV (using our best estimate of the heat of formation and ionization potential of  $\text{NH}$  discussed later). Clearly, interference of these two processes makes interpretation difficult and the results of Reed and Sneddon, including  $\Delta H_{f,0}^\circ(\text{NH})$  in Table 4, should be disregarded. The latter process cannot be of importance in Gibson, et al.'s, experiment because there is no  $\text{NH}_3$  present.

The results of Ervin and Armentrout were based on kinetics measurements for the reaction  $\text{N}^+ + \text{H}_2 + \text{NH}^+ + \text{H}$ . There have also been three previous studies of the kinetics of this reaction.<sup>97-99</sup> All have shown that the reaction has a very small activation energy. In one of these,<sup>97</sup> isotopic studies have clearly shown that the activation energy is entirely due to the reaction's very slight endothermicity. The thermochemical results follow from this fortuitous circumstance. However, there is a minor problem with the first three experiments of this type. As pointed out by Ervin and Armentrout, the rotational energy of  $\text{H}_2$  is of the order of the reaction endothermicity and a correction must therefore be made for it in low temperature experiments. (The basic question is, what are the relative amounts of ortho and para hydrogen and how does the ratio affect the results?) In Refs. 98 and 99 the correction for the rotational energy was made simply by subtracting it from the energy available for reaction. It is possible that not all of the rotational energy is effective in driving the reaction, so that this is an overcorrection. Ervin and Armentrout used three different models to estimate the importance of the rotational energy and determine error limits for the resulting heat of formation. It is worth noting that the other three results for the reaction endothermicity agree with that of Ervin and Armentrout within error limits after they are corrected for zero point energy by simple subtraction of the excess rotational energy.<sup>75</sup> However, their error limits are quite small in comparison because possible errors in the rotational energy correction were not considered. Therefore, the result of Ervin and Armentrout

was chosen as the best of this type of experiment. Their result for the  $\text{NH}^+$  heat of formation was  $396.8 \pm 0.6$  kcal/mole, in excellent agreement with Gibson, et al.

Having the heat of formation from two types of experiments for  $\text{NH}^+$ , the ionization potential of  $\text{NH}$  is needed to calculate the heat of formation of  $\text{NH}$ . Since the value recommended here relies heavily on this IP, some discussion of the selection is in order. The earliest measurement of this IP was by Reed and Sneddon<sup>62</sup> in 1959. They found a value  $13.1 \pm 0.05$  eV by electron impact measurements on  $\text{NH}_3$ . Foner and Hudson<sup>100</sup> later (1966) performed similar experiments and found a value  $13.1 \pm 0.2$  eV. Still later (1981) Foner and Hudson<sup>101</sup> performed electron impact measurements on  $\text{NH}$  produced by the reaction of  $\text{F}$  with  $\text{NH}_3$ . Their new value was  $13.47 \pm 0.05$  eV. They pointed out that their earlier technique<sup>100</sup> had some problems with the formation of  $\text{NH}$  in the  $a^1\Delta$  state which led to the large error limits in the result. They also questioned the error limits on Reed and Sneddon's result. Since the formation of  $\text{NH } a^1\Delta$  could also affect Reed and Sneddon's result, this value clearly is not the best to use. It would appear that the best value to use is from the photoionization work of Dunlavey, et al.<sup>57</sup> Their result was  $13.49 \pm 0.01$  eV which agrees well with the most recent result of Foner and Hudson. This value comes from a single peak observed in the range 13.0 - 13.5 eV. There was no interference from other spectra as happened for the  $\text{NH}_3 \rightarrow \text{NH}_2^+ + \text{H} + \text{e}^-$  reaction (see previous section). In addition, by varying the ratio of  $\text{NH}$  and  $\text{NH}_2$  concentrations it was possible to prove that this peak is not due to  $\text{NH}_2$ . This would therefore appear to be a firm result for the  $\text{NH}$  ionization potential.

Both Gibson, et al., and Ervin and Armentrout used Dunlavey, et al.'s, ionization potential in their thermochemical calculations. Their results for the  $\text{NH}$  heat of formation were  $85.2 \pm 0.4$  and  $85.8 \pm 0.6$  kcal/mole, respectively. There appears to be no reason to favor either the results of Gibson, et al., or of Ervin and Armentrout. Therefore, after critical evaluation of all available measurements, the weighted average<sup>59</sup> of these two results,  $85.4 \pm 0.3$  kcal/mole, is given as the recommended value from this survey. Note that this result is in good agreement with most of the recent theoretical calculations (see Table 6).

Two of the flame results for the  $\text{NH}$  heat of formation, that of Kaskan and Nadler<sup>7</sup> and of Fisher,<sup>8</sup> are in good agreement with the recommended value (see Table 5). However, the results for two flames studied by Chou, Dean, and Stern<sup>10</sup> are much too high. It is believed that the recommended value has a strong enough basis to be used as a test of the validity of the flame results. Therefore, the result of Chou, Dean, and Stern appears to be in error. It is not clear why a systematic error should be present in their results. The burner used in their work was very similar to those used by Kaskan and Nadler and by Fisher.\* These burners used shrouded flows, that is, the premixed  $\text{NH}_3$

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\*It should be noted here that the experiments of Fisher were not independent from those of Kaskan and coworkers. In fact, Fisher was strongly influenced by these results since he was a postdoctoral associate of Kaskan. During Fisher's early tenure, Kaskan died. Fisher then carried on the research and was sole author of Ref. 8. Fisher used similar methods to those of Ref. 7.

and  $O_2$  flowed through a central core of the burner while  $N_2$  flowed around the central core to prevent room air from entering the flow. Care was taken to insure that turbulent mixing did not occur between the flowing gas layers. Therefore, it appears unlikely that mixing with room air could have caused problems. All of the raw absorption data for the individual species in R1-R3 which were measured by Chou, Dean, and Stern were provided in Ref. 10. A cross check of their results was performed at a few points for each species.\* No discrepancies were found with their data reduction. Possibly the best explanation may be that measurements of the different species had to be performed one at a time with large time intervals between each to allow for changing of laser dyes and wavelengths. The concentrations of trace species could be extremely sensitive to experimental conditions such as flame temperature. If these changed somewhat between species measurements, this might explain the discrepancy.\*\* (In considering such possible effects, it is worth noting that the calculation of  $\Delta H_{f,0}^\circ$  includes the term  $\Delta G_r = -RT \ln(K_{3,eq})$ . At typical temperatures of the flames used,  $\Delta G_r \sim -(4 \text{ kcal/mole}) \ln(K_{3,eq})$ . A factor of  $\sim 2$  error in the concentrations of  $NH$  or  $NH_3$  or  $\sim 1.5$  error in the concentration of  $OH$  would thus produce an error of about 3 kcal/mole in the result for  $\Delta H_{f,0}^\circ$ ). Measurements in Refs. 7 and 8 were probably made in a much shorter time span than in Ref. 10 because a Xe arc lamp source and monochromator were used for the absorption measurements. All of the wavelengths necessary to probe the species of interest were readily available with this system simply by tuning the monochromator.

#### IV. COMPARISON OF EXPERIMENTAL AND CALCULATED $NH_2$ OSCILLATOR STRENGTHS

In Refs. 7, 8, and 10 measured values are presented for oscillator strengths of two transitions of  $NH_2$ . Having, we believe, more accurate values for the heats of formation of  $NH$  and  $NH_2$  available, we proceeded to correct the results for the new thermodynamic data. In addition, the results were also corrected for the more accurate oscillator strengths of the relevant  $NH$  and  $OH$  transitions currently available. The latter corrections were large for results of Refs. 7 and 8, but small for Ref. 10 because the correct value of the  $OH$  oscillator strength was used in Ref. 10. In Ref. 7 the equilibrium of R1 is used, while in Refs. 8 and 10 the equilibrium of R2 is used. In Refs. 7 and 8 the transition studied was the  $R_{Q_0,N^4}$  in the  $(0,12,0)\Pi - (0,0,0)$  band. Data of Ref. 7 for the two flames which were studied lead to values of  $2.81 \pm 0.47 \times 10^{-4}$  (flame 1) and  $2.8 \pm 1.2 \times 10^{-4}$  (flame 2) for the oscillator strength of this transition. Data of Ref. 8 leads to the value  $3.80 \pm 0.85 \times 10^{-4}$ . The calculated value is  $2.84 \pm 0.28 \times 10^{-4}$ , in good agreement. (Normalized linestrengths used in the calculations for the transitions discussed in this section are given in Table 8). However, the results of Ref. 10 lead to an oscillator strength which does not agree nearly so well with calculated results. There, the oscillator strength for the  $P_{Q_1,N^7}$  transition

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\*We are indebted to A.M. Dean and M.S. Chou for providing their measured values of the ratio of peak height to integrated peak area for each compound studied in Ref. 10. These ratios are close to what one would expect for optically thin conditions upon considering the linewidth of the laser used ( $\sim 0.3 \text{ cm}^{-1}$ ) and Doppler width of the transitions.

\*\*It should be noted that the authors of Ref. 10 do not agree that experimental conditions could have changed significantly.<sup>102</sup>

in the  $(0,9,0)\Sigma - (0,0,0)$  band was measured. Results for two flames lead to measured values for this oscillator strength of  $5.3 \pm 1.6 \times 10^{-5}$  (flame 1) and  $3.9 \pm 1.2 \times 10^{-5}$  (flame 3). Our calculated value is  $1.96 \pm 0.20 \times 10^{-4}$ . We are unable to explain the disagreement by about a factor of 4. However, the fact that there is disagreement between the NH heat of formation derived from results in Ref. 10 and the value recommended from the present literature review suggests that the results of Ref. 10 cannot be trusted in such a quantitatively demanding fashion as required for the oscillator strength comparison.\*

Table 8. Calculated Linestrength Factors for Selected  $\text{NH}_2$  Transitions  
(Normalized Properly for Absorption)

Rotational Transition	Vibrational Band	$S_{N',N''}/(2N''+1)$
$R_{Q_0,N^4}$	$(0,12,0)\Pi - (0,0,0)$	0.709
$P_{Q_1,N^7}$	$(0,9,0)\Sigma - (0,0,0)$	0.451
$R_{R_0,N^1}$	$(0,12,0)\Pi - (0,0,0)$ $(0,10,0)\Pi - (0,0,0)$ $(1,8,0)\Pi - (0,0,0)$	0.500
$R_{Q_0,N^1}$	$(0,12,0)\Pi - (0,0,0)$ $(0,10,0)\Pi - (0,0,0)$ $(1,8,0)\Pi - (0,0,0)$	0.500

No other absolute measurements of  $\text{NH}_2$  oscillator strengths are available. However, two relative measurements can be derived from data in Ref. 15. In Ref. 15, measurements of the  $R_{R_0,N^1}$  and  $R_{Q_0,N^1}$  transitions in three different vibrational bands show that the relative intensities of these two types of transitions is 1:1. Our calculated linestrengths also predict this result. Unfortunately, this is not a very stringent test. Perusal of tables in Ref. 18 for the case of equal ground and excited state asymmetry parameters shows that at this low value of the rotational quantum number, N, there is no variation of the ratio with asymmetry parameter (i.e., bending angle).

## V. CONCLUSIONS

The main thrust of this work was to provide a critical comparison of measured  $\text{NH}_2$  oscillator strengths to our calculated values. For this purpose, a critical review of the heats of formation of NH and  $\text{NH}_2$  had to be performed.

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\*This author does not believe that the systematic error suggested here is sufficiently large to change any of the qualitative interpretations of Ref. 10 concerning, for instance, the  $\text{NH}_3/\text{O}_2$  flame chemistry.

The review leads to recommended values ( $0^\circ\text{K}$ ) for  $\text{NH}$  and  $\text{NH}_2$  of  $85.4 \pm 0.3$  kcal/mole and  $75.9 \pm 0.2$  kcal/mole, respectively. These heats of formation were used with other data from the literature to determine measured absolute oscillator strengths of  $\text{NH}_2$  for two transitions. Agreement between measured and calculated results for one of the transitions is good, but rather poor for the other. However, the measurements which are in poor agreement with our calculated value also yielded an  $\text{NH}$  heat of formation in poor agreement with that recommended from the literature survey. It is therefore suggested that systematic errors in the measured results lead to the discrepancy in measured and calculated oscillator strengths for this transition. One experiment has led to relative intensities of a few rotational lines which agree with our calculations. Unfortunately, there are simply not enough measurements to provide a very stringent test of our calculational method. What measurements can be made to remedy the situation? The lifetimes of the excited vibrational levels are now very well known. Therefore, the only questions remaining concern the validity of the FCF and rotational linestrength calculations. These may be checked by relative intensity measurements of vibrational bands and rotational lines of the  $\text{NH}_2$  A-X transition. LIF experiments along these lines are planned for the near future.

#### ACKNOWLEDGEMENTS

The author thanks R.M. Greene for sending data concerning Ref. 9 and J. Sutherland for sending a preprint of his work. The author is also indebted to A. Dean, M.S. Chou, and J. Berkowitz for helpful and encouraging discussions. The author is grateful to A.J. Kotlar for calculating the linestrengths of  $\text{NH}_2$  necessary to perform the comparisons in this paper and for several insightful discussions. The author is also appreciative to A.J. Kotlar and D.R. Crosley for their critical readings of the manuscript.

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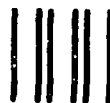
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